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Evaluation of a Passive Monitor for Volatile Organics

Battelle Columbus Labs., OH

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FINAL REPORT

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EVALUATION OF A PASSIVE MONITOR FOR VOLATILE ORGANICS

by

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16. ABSTRACT

A laboratory investigation was conducted to determine the potential utility of a commercially available passive dosimeter for monitoring toxic volatile organic compounds at ambient levels. Test compounds included: chloroform, methylchloroform, carbon tetrachloride, trichloroethylene, tetrachloroethylene, benzene, and chlorobenzene.

Feasibility for reduction in device blanks was demonstrated and improvements were made in the analytical procedures. Chamber tests of device performance showed generally good performance at ambient levels, but indicated a severe limitation in sampling ability at relative humidities greater than about 80 percent. Also, generally low results were obtained with carbon tetrachloride. The cause of the observed effect of air velocity on sampling rates was examined on a theoretical basis, and it is recommended that these devices not be employed without adequate ventilation.

It is concluded that at least one currently available passive dosimeter could be useful for monitoring of ambient levels of toxic organic chemicals, and appropriate precautions are indicated.

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air, Noise, and Radiation, the Office of Toxic Substances, and the Office of Enforcement.

The determination of human exposure to toxic organic compounds is an area of increasing importance to EPA. The passive personal monitors evaluated in this study are possible candidate devices to be employed in future exposure monitoring studies. These devices are presently being employed in industrial hygiene studies and have many characteristics which make them potentially very useful in ambient air investigations. However, since the requirements for ambient air monitoring are more stringent than those for industrial hygiene, the present investigation was undertaken to identify possible problems with the commercially available devices where they are used in ambient air studies. Once identified, potential weaknesses may be corrected, resulting in valid use of the passive monitors in ambient exposure monitoring.

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ABSTRACT

A laboratory investigation was conducted to determine the potential utility of selected commercially available passive dosimeters for monitoring toxic volatile organic compounds at ambient levels. The test compounds included: chloroform, methylchloroform, carbon tetrachloride, trichloroethylene, tetrachloroethylene, benzene, and chlorobenzene.

Problems associated with high and variable blank levels and analytical detection limits relative to the use of these devices for ambient level monitoring were identified in a previous program (1). In the current program, cooperative efforts with manufacturers demonstrated the feasibility for minimization of the blank problem, and improvements were made in the analytical procedures.

It also was demonstrated that blank levels for at least one commercially available device, the Pro-Tek G-AA air monitoring badge made by DuPont, can be limited to near or below the analytical detection limits and within tentative requirements for ambient sampling for the test set of chemicals.

Chamber tests were conducted to determine the performance of the DuPont device. These tests showed that performance is independent of concentration at normal ambient levels, and that performance is significantly impaired by relative humidities of the order of 80 percent and higher. Statistical analysis of the results suggests that much of the observed variance in the data can be attributed to variable sampling rates possibly caused by leakage of the individual devices. Manufacturers' specified sampling rates were reasonably accurate for most of the compounds, but in the case of carbon tetrachloride consistently low results were obtained.

Results of a theoretical treatment of the effect of air velocity on sampling rate are consistent with experimental results obtained by the manufacturer, and it is recommended that these devices not be used without sufficient ventilation as defined by the results (velocities less than about 30 fpm).

It is concluded that at least one currently available passive monitor could be useful for semiquantitative ambient monitoring of toxic organic chemicals. However, care must be taken in specification of devices having low blanks. Improved quality control could eliminate much of the observed variation in sampling rates, and in some cases sampling rates for individual chemicals may need to be re-evaluated. Field evaluation of the devices in comparison with other existing methodologies is recommended.

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SECTION 1

INTRODUCTION

In recent years an increased awareness of the need for monitoring of individual or personal exposures to pollutants and toxic chemicals of various types has evolved. This awareness has prompted the development of a variety of personal sampling devices including battery driven pump systems (active systems), passive systems having high specificity for individual compounds, and generalized passive systems intended for collection of volatile organic compounds. Initial applications of these various devices have been concerned with the relatively high concentrations of contaminants found in industrial workplaces. In an earlier program conducted for the Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina (RTP), Battelle's Columbus Laboratories (BCL) explored the problems and limitations associated with the potential use of passive devices for monitoring ambient level toxic organic chemicals (1). In that prior program (1), several commercially available passive monitors were examined with respect to potential problems in attempting to adapt them to use under ambient sampling conditions. In brief, the major problem with use of those devices was found to be the excessively high and variable blank levels for several of the chlorinated hydrocarbons. These blanks were different for devices produced by different manufacturers, and comments concerning the applicability of the devices to ambient level monitoring were given. In addition, some problems related to the analytical procedures employed with these devices were noted. This current Work Assignment was concerned with the alleviation of some of the problems associated with this application of passive monitors and with a laboratory level evaluation of the performance of one passive monitor at ambient concentrations.

The objective of this task was to evaluate the utility of selected passive monitors for their applicability to 24-hour monitoring of volatile organic compounds at typical ambient concentration levels. Seven target compounds that are representative of volatile toxic chemicals relevant to EPA monitoring requirements were considered. These included chloroform, 1,1,1-trichloroethane, carbon tetrachloride, trichloroethylene, tetrachloroethylene, benzene, and chlorobenzene.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

Previous work (1) had shown that the major limitations for the use of commercially available passive monitors for collection of toxic organic compounds from ambient air were related primarily to the high and variable blank levels for several chlorinated hydrocarbons and to the analytical detectability of certain compounds. In the current work, improvements were made in the analytical methodology through the use of capillary column chromatographic techniques. One manufacturer, DuPont, elected to investigate possible sources of blank contamination, and it was demonstrated that sufficiently low blanks can be obtained without additional manufacturing costs. Laboratory evaluation of these improved devices lead to the following specific conclusions:

(1) When appropriate care is taken to minimize exposure of collector strips to contaminated air during processing, blank levels for the chlorinated hydrocarbons on the DuPont devices are near to or below detection levels for all compounds of interest.

(2) Thermal desorption is not a viable approach for analysis of the DuPont badges.

(3) Both resolution and detectability are improved relative to previous results through the use of capillary column chromatography.

(4) Chamber tests of badge performance show:

   a. Badge performance is not a function of concentration at levels as low as 0.03 ppbv for the test chemicals.

   b. Badge performance is not affected by relative humidity at humidity levels up to about 80 percent, but sampling is severely impaired at levels of 80 percent and higher.

c. Much of the variance in the data can be attributed to badge variability (sampling rates), with occasional examples of errors of 50 to 80 percent being observed.

d. Relative performance values are reasonably consistent for any given compound, but tend to show some scatter from one compound to another. This is most marked for CCl_4 for which the apparent overall efficiency of collection and analysis was only about 70 percent. This could reflect a constant inaccuracy in either the desorption efficiency or in the sampling rate supplied by DuPont.

(5) Passive devices do not function accurately when sufficient ventilation is not provided, and this air velocity effect needs to be considered relative to the mechanics of intended applications.

Although reasonable relative standard deviations of 10 to 30 percent were observed in the current laboratory evaluation, it is likely that some improvement in these values could be obtained. One major improvement would result from better control of the construction of the devices and hence better control of sampling rates. This is especially important when consideration is made of the potential effects of field sampling on overall accuracy. Under field conditions, collected samples are likely to be much more complex than the simple mixtures examined in this program. In such cases, the effective analytical accuracy and precision may be impaired, at least for some compounds.

These considerations also lead to the recommendation that the passive devices should be further evaluated under field conditions. Such tests should be conducted with comparison of passive devices to available active systems, and wherever possible direct analysis should be employed as the primary reference. This could be done by either periodic chromatographic analysis or time-averaging gas-sampling techniques. A combination of these techniques probably could be designed to yield the most meaningful overall results.

SECTION 3

TECHNICAL BACKGROUND

PASSIVE MONITOR FUNDAMENTALS

Passive monitors are available based on two general modes of operation: (1) diffusion limited sampling, and (2) permeation limited sampling. In each case a collector or sorbent material is separated from the external environment by a physical barrier that determines the sampling characteristics of the device. Permeation limited devices employ a membrane in which the compounds of interest are soluble. Because of this solubility requirement, it is possible to achieve some selectivity with permeation devices via choice of the membrane material. However, because of the variability of solubility even within an homologous series of compounds, permeation devices must be calibrated for each individual chemical that is sampled.

With diffusion limited devices, the collector is isolated from the environment by a porous barrier containing a well-defined series of channels or pores. The purpose of these channels is to provide a geometrically well-defined zone of essentially quiescent space through which mass transport is achieved solely by diffusion. As a general criterion for this condition, the length/diameter ratio (L/d) of the pores should be at least 3. Under such conditions, the mass flow rate to the collector is given by Fick's first law, viz.,

$$\dot{m} = (DA/L)(C_{\infty} - C_o) \quad , \qquad (1)$$

where D is the diffusion coefficient for the species of interest, A is the total channel area of the device, L is the channel length, C_{∞} is the external concentration of the species and C_o is the concentration at the surface of the collector. If the collector has any appreciable efficiency for sorption of the compound of interest, C_o is generally taken to be zero.

It should be noted that the quantity DA/L has units of volume/time. This quantity is often referred to as the sampling rate of the device. It would be preferable if the sampling rate of a given device could be determined independently of its use for monitoring purposes. This is not possible, however, and one must rely on the manufacturer's specifications of A/L and/or DA/L. Lautenberger, et al. (2) claim that values of A/L for the DuPont badges are precise to $\pm$ 5 percent. Values of DA/L given by the DuPont brochure (supplied with the badges) are based partly on independent sampling

rates measured directly with their badges, but no measure of the expected variation in sampling rates is given.

Reid, Prausnitz, and Sherwood (3) give an excellent review of methods for estimating diffusion coefficients, as might be necessary when dealing with chemicals not covered by the manufacturer's brochure, and they also comment on some of the difficulties that limit accuracy and precision in the experimental determination of diffusion coefficients. These authors estimate that experimental diffusion coefficients are often probably high by a few percent because of the difficulty in eliminating convection during the measurement. The best procedure for estimating diffusion coefficients, according to Reid, et al (3), is an empirical correlation due to Fuller, Schettler, and Giddings (4)(FSG). For 109 data points, the FSG method yielded an average relative error of 0.54 percent $\pm$ 8.7 percent. Thus, the overall accuracy (bias + 2 x coefficient of variation) for sampling rates may be expected to be of the order of 13 to 28 percent depending on how these rates are obtained.

Values of sampling rates specified by DuPont for the test set of chemicals for this program in comparison with those calculated by the FSG method (A/L = 14.8) are shown in Table 1. Some discrepancies are noted in this comparison, and further comment will be made under the discussion of experimental data obtained on this program.

VELOCITY EFFECTS

It also should be noted that sampling rates for a passive monitor are dependent on the air velocity over the face of the device. Under normal sampling conditions where velocities of around 50 to 200 fpm are encountered, sampling rates are relatively independent of velocity, but at velocities lower than about 30-50 fpm, the sampling rate is diminished significantly. Appendix A is a further discussion of the effect of velocity on sampling rate.

TEMPERATURE EFFECTS

In the case of diffusion limited devices, the temperature effect is relatively straightforward. Although kinetic gas theory suggests that the diffusion coefficient is proportional to $T^{1.5}$, empirical correlations such as FSG usually show better results using $T^{1.75}$.

TABLE 1. SAMPLING RATES[a]
(at 25 C)

Compound	R_{DP}[b], cc/min	R_{FSG}, cc/min	DP/FSG
Chloroform	79.0	80.8	0.98
1,1,1-trichloroethane (Methylchloroform)	60.4	72.6	0.83
Carbon Tetrachloride	73.6	72.6	1.01
Trichloroethylene	65.2	73.9	0.88
Tetrachloroethylene	51.0	67.5	0.76
Benzene	71.4	79.4	0.90
Chlorobenzene	66.4	70.6	0.94

(a) DuPont type G-AA badge with both faces exposed.

(b) DuPont brochure, 1980 with selected values revised by personal communication, 1981.

SECTION 4

OBJECTIVE

The objective of the current Work Assignment was to further explore the applicability of commercially available diffusion limited devices for monitoring toxic organic substances at ambient levels. Specific goals of the program included:

(1) Cooperative efforts with manufacturers to explore the feasibility of reduction of blanks without compromising the proprietary nature of the sorbents.

(2) Refinement of analytical techniques, including identification of potential interferences.

(3) Chamber tests of devices having sufficiently low blanks for:

   a. concentration effects

   b. relative humidity effects

   c. temperature effects

   d. velocity effects.

(4) Limited evaluation of device performance in real ambient atmospheres (laboratory).

SECTION 5

EXPERIMENTAL METHODS

ANALYSIS PROCEDURES

Gas Chromatograph

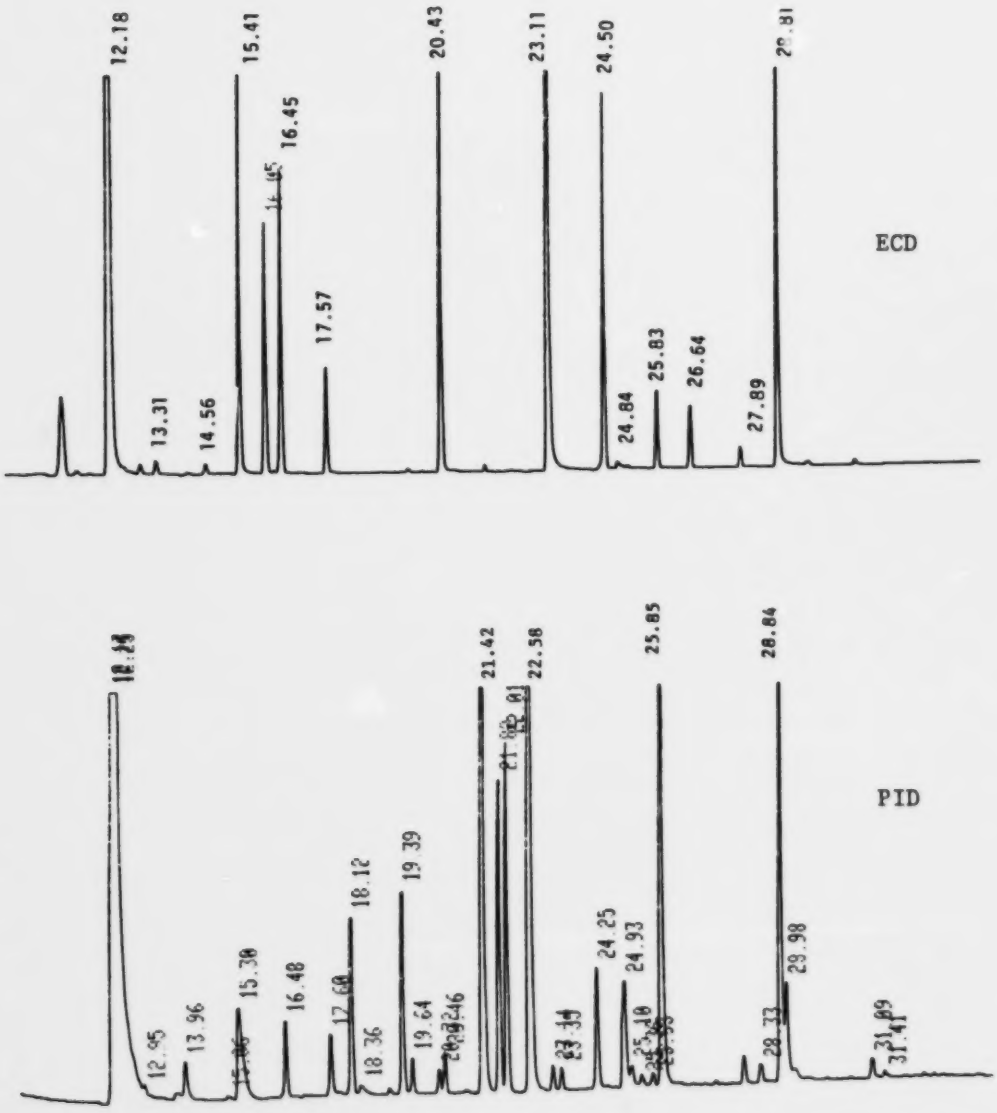
Analyses for this program were carried out using a Varian Model 3700 gas chromatograph coupled to two Hewlett-Packard Model 3380 integrators for data readout. Midway through the program a Hewlett-Packard Model 3390 integrator was added to the system to facilitate readout of complex laboratory and simulated laboratory air mixtures. Component detection was accomplished using the series combination of electron capture and photoionization detectors described previously (1).

Columns--

Initial results on this program were obtained using Carbopack-B (with 1 percent SP-1000) as previously described. In an effort to improve the overall quality of the analytical system, a changeover was made to the use of Hewlett-Packard fused silica capillary columns. A 25-m SE-30 coated column was used for gas analyses, and a 50-m SE-30 column was used for analysis of liquid samples. The gas analysis column was operated in a splitless mode, with cryogenic on-column trapping of a 10-cc gas sample to achieve the required sensitivity. The liquid analysis column was operated with inlet split ratios of 10-20, with the Carbopack-B column being retained for supply of makeup gas and verification of split ratios. Each column therefore had a separate inlet, but all three were common at the detector inlet. This arrangement facilitated rapid changeover in sample types, and the potential loss in sensitivity due to use of split input of liquid samples to the capillary was more than offset by gains in peak resolution and signal-to-noise ratio. Dual chromatograms obtained with the capillary system for the subject compounds are shown in Figure 1. These chromatograms show compounds additional to the base set used in this program and illustrate the separation of the base set from other common organic compounds. Indeed, additional compounds were examined in some of the tests, but only the base set was universally examined.

Desorption

All samples analyzed in this program were desorbed by solvent desorption techniques using 5 percent carbon disulfide in methanol as the desorbing



Sample: Spiked air
Run Conditions: Volume = 10cc
Column = 24m fused silica capillary
Flow Rate = 1 cc/min @ 25 C
Temperature = 5 min @ -80 C; 8 C/min to 150 C

Output Key: see Table 2

FIGURE 1. DUAL CHROMATOGRAM OF GAS SAMPLE

TABLE 2. KEY TO CHEMICALS IN FIGURE 1

Chemical	Retention Time, min.	Detector[a] ECD	Detector[a] PID	Approximate[b] Concentration, ppbv of Run	DL, ppbv
Chloroform	15.41	X	-	130	0.08
Methylchloroform	16.05	X	x	25	0.02
Carbon tetrachloride	16.45	X	-	4	0.005
Trichloro-ethylene	17.57	X	X	23	0.06
Tetrachloro-ethylene	20.43	X	X	27	0.01
1,1,2,2-Tetra-chloroethane	23.11	X	x	>58	(0.01)
1,1,1,2-Tetra-chloroethane	24.50	X	x	(27)	(0.01)
p-dichloro-benzene	24.84	x	-	-	-
o-dichloro-benzene	25.83	X	-	-	-
1,3,5-trichloro-benzene	27.89	x	-	-	-
1,2,4-trichloro-benzene	28.81	x	-	-	-
Benzene	16.48	-	X	3.6	0.1
Methylcyclo-hexane	20.46	-	x	-	-
Toluene	19.39	-	X	(10)	(0.1)
Chlorobenzene	21.42	-	x	36	0.13
Ethylbenzene	21.82	-	X	(15)	(0.1)
m&p-xylene	22.01	-	X	(16)	(0.1)
p-ethyltoluene	24.25	-	X	(6)	(0.1)
1,2,4-trimethyl-benzene	28.84	-	X	(37)	(0.1)

(a) X = good response; x = fair response; - = poor response.
(b) Estimated concentrations and detection limits in parentheses; - indicates no basis for estimate.

agent. Procedures, precautions, and methods for determination of desorption efficiencies have been described previously (1).

Because of the desirability, in some cases, for the use of thermal desorption, this technique also was used for many of the collector samples generated in the chamber tests on this program. In applying this technique, small portions (ca 1/40) of the collector were removed from the bulk collector strip. These small portions then were used for thermal desorption, while the bulk of the strip was subjected to solvent desorption. Subsequent analytical results were corrected for the mass of collector employed in each technique. Collector segments that were analyzed by thermal desorption were inserted into a standard glass injection port liner that could then be placed in a spare injector. This injector was equipped with a rapid-rise heater and temperature readout system that was separate from the normal GC system. Samples were heated to 300 C for 10 minutes, and the vapors were cryogenically trapped on-column. This temperature was chosen because of the fact that it is used by the manufacturer for thermal cleanup of the devices. Various time periods were tried, with the result that 10 minutes appeared to be sufficient.

CHAMBER TEST PROCEDURES

Test Chamber

The chamber used for device exposure studies is shown in Figure 2. This chamber is a 200-L glass chamber constructed from two opposing bell jars that are joined to a central anodized aluminum ring. This ring is provided with numerous ports for loading, sampling, monitoring devices, etc. Stirring within the chamber is achieved using a completely sealed internal fan that is magnetically coupled to an external variable speed drive unit. For the current experiments, a stainless steel shroud and swirl dampener was placed over the fan in order to achieve well-directed flow within the chamber and a uniform flow pattern in the vicinity of the devices.

Devices were loaded into the chamber using the sample holder shown in Figure 3. This holder is a stainless steel cylinder with a central rod for attachment of the passive devices. For any experiment, the devices could be attached to the holder under a protective clean atmosphere; the cylinder was closed and was flushed with zero nitrogen; and the cylinder was inserted into the chamber, with one end locked in place while the other end protruded through a seal in the aluminum ring. The concentrations of test species could then be adjusted in the chamber without exposure of the badges. At the start of a chamber exposure, the outer shell of the cylinder was partially withdrawn through the seal, leaving the badges suspended from the central rod. At the completion of the run, this procedure was reversed, and the entire assembly was removed to a glove box for disassembly and preparation of the collectors for analysis.

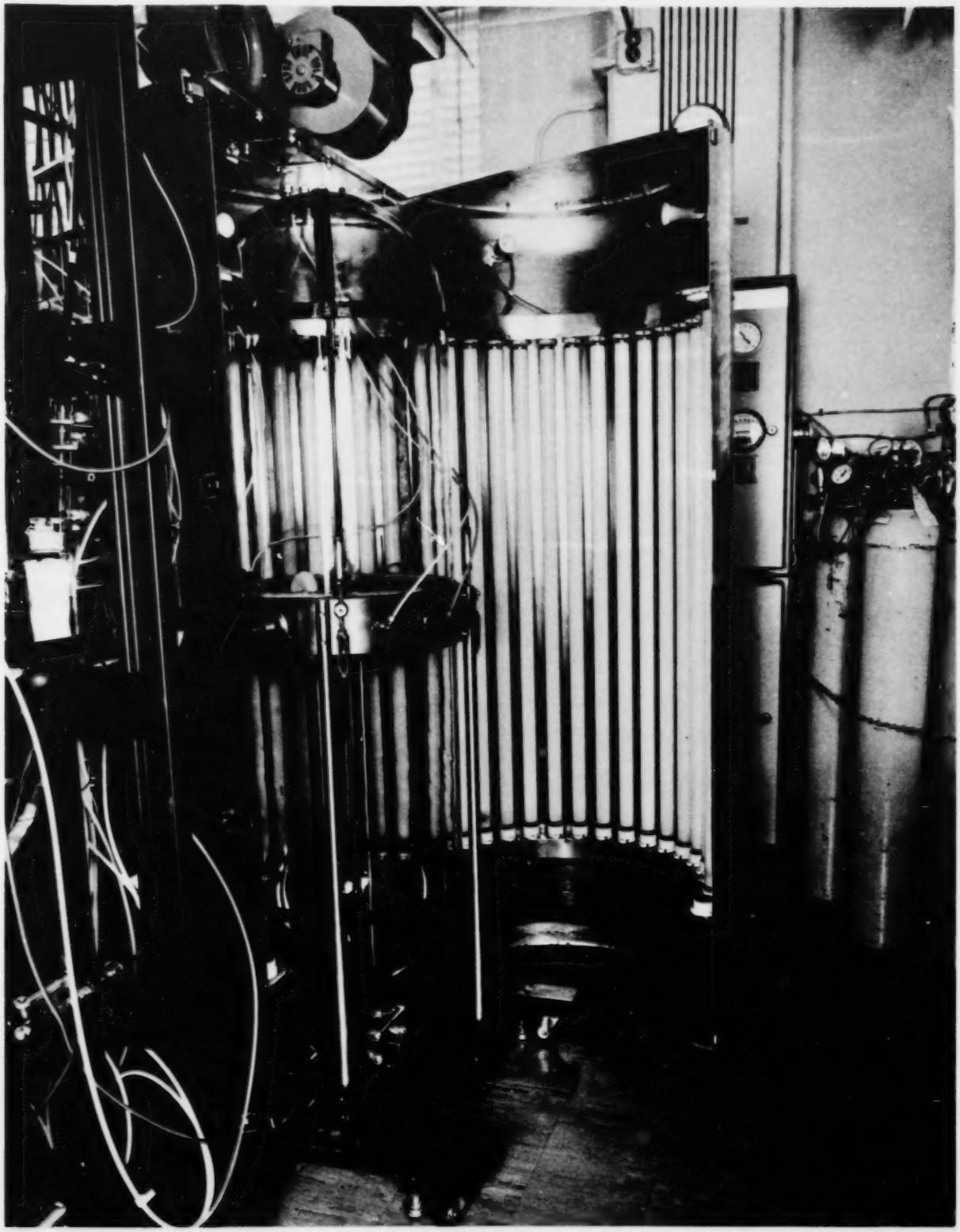


FIGURE 2. EXPOSURE CHAMBER

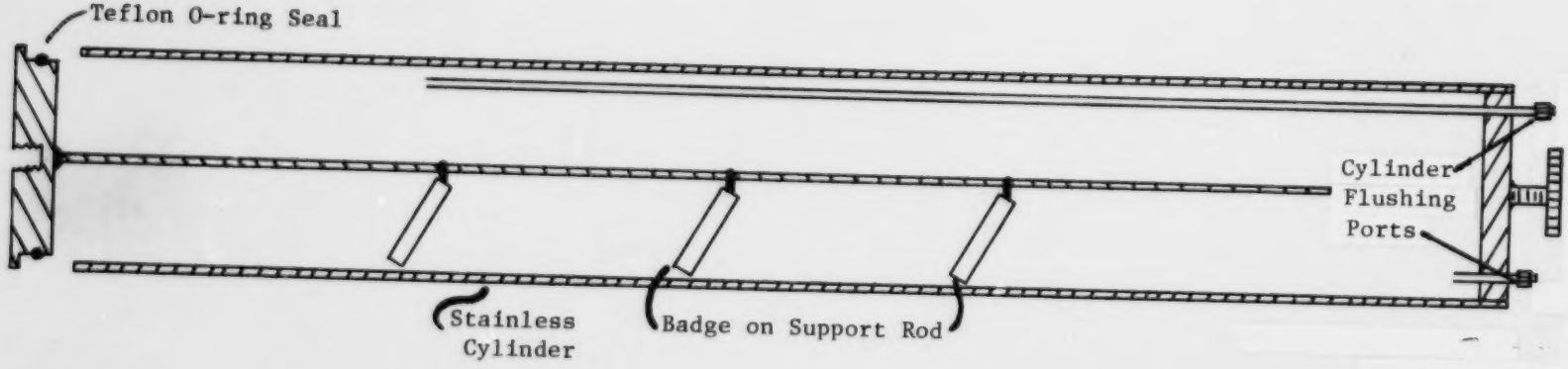


FIGURE 3. BADGE LOADING AND SUPPORT DEVICE FOR CHAMBER TESTS

Prior to each chamber run, the chamber was thoroughly flushed with zero nitrogen and gas analyses were made by GC to confirm the initial condition of the chamber. Addition of the test species was made by direct injection of an appropriate liquid or gas mixture of the pure chemicals. Dilution then was carried out in the chamber as needed to obtain the desired concentrations. Once loaded, the chamber was operated in a dynamic mode with about 50 cc/min of gas being removed for GC analysis and appropriate makeup gas being added to maintain the chamber at about 1.0 in. H_2O above ambient pressure. Velocity measurements were made using an Alnor anemometer. Details of the chamber test procedure are outlined in Appendix B.

SECTION 6

EXPERIMENTAL RESULTS

DEVICE BLANKS

Based on results obtained in a previous program (1) representatives of both DuPont and 3M were asked to review manufacturing and packaging procedures for their passive devices in an attempt to identify and eliminate the high and variable blanks found with these badges. It was determined that packaging procedures used by 3M had been changed since our original examination of these badges, and a number of new badges were obtained for analysis. Blank levels for these badges were below detection limits for all compounds of interest except trichloroethylene and methylchloroform. Levels for these two compounds were approximately 190 and 160 ng/badge, respectively. Although these levels are approximately 30 percent lower than previously observed with the 3M badges, they are still too high with respect to projected 24-hour ambient level sampling needs. 3M representatives did not offer to pursue this problem further and no further examination of 3M devices was made.

The initial set of samples received from DuPont consisted of only the collectors and these were provided in screw-top vials having aluminum cap liners. These collectors were in four groups that were thermally cleaned by DuPont at 300 C for 3, 4, 5, and 6 hours, respectively. In processing these collectors for analysis we handled collectors numbered 1, 2, and (3 + 4) as three separate groups, whereas collectors having similar letter designations (A, B, C, D) were processed separately by DuPont (see Table 3). In this way we attempted to distinguish between possible sources of contamination resulting from our handling of the collectors and those contributed by DuPont. In all cases, compounds other than those of interest to this program were noted for this series of badges. Inasmuch as the A group of collectors showed very high levels of other compounds, it was concluded, with the concurrence of the manufacturer, that these collectors had not received sufficient heat treatment, and only two collectors from this group were analyzed. The other three letter groups showed examples of both contaminated and relatively clean collectors. Indeed, collectors B-3 and D-3 had extremely high levels of benzene, whereas collectors B-4 and D-4 were two of the cleanest collectors that we had examined to this point. Evidence of relatively clean collectors was seen with each of the three longer heat-treat

TABLE 3. SPECIAL DUPONT BLANKS (ng/badge) [a]

Compound[b]	A[c]		B				C				D			
	1	2	1	2	3	4	1	2	3	4	1	2	3	4
Chloroform	144	<5[d]	<5	<5	113	<5	<5	<5	<5	<5	86	22	95	<5
1,1,1-trichlorethane	15	10	<2	7	55	<2	8	9	11	<2	14	7	37	8
Carbon tetrachloride	66	1	4	1	135	<0.4	1	6	<0.4	7	61	11	104	<0.4
Trichloroethylene	<4	360	56	51	<4	<4	83	44	21	<4	35	<4	<4	<4
Tetrachloroethylene	<0.7	(1)[e]	<0.7	(1)	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	<0.7	(1)	<0.7	3
Benzene	<10	<10	<10	<10	2400	<10	<10	<10	<10	<10	<10	<10	2200	<10
Chlorobenzene	<18	<18	<18	<18	<18	<18	<18	<18	<18	<18	<18	<18	<18	<18

(a) Concentrations corrected for solvent blanks but not for desorption efficiencies.
(b) Compounds identified; other compounds not on project list and not identified are seen in all cases.
(c) Heat treat period: A = 3 hrs.; B = 4 hrs.; C = 5 hrs.; D = 6 hrs., at 300 C.
(d) <N = less than detection limit of N.
(e) Questionable value, close to detection limit.

periods, but the evidence in Table 3 does not consistently reflect either our handling or processing by DuPont as the source of observed variations in contamination levels.

Since the results shown in Table 3 suggest that clean badges could indeed be produced, DuPont agreed to prepare two additional sets of badges for further evaluation of blanks. Both sets of collectors were initially processed in the same way, with a 4-hour heat soak at 300 C in an air circulation oven. During this treatment clean air rather than normal plant air was supplied to the oven. The collectors were then cooled and one half of them were packaged in glass vials. The other half of the batch was packaged in standard holders and foil envelopes that had been subjected to mild thermal cleanup. Blank levels found in these two types of samples are shown in Tables 4 and 5. The collectors that were packaged in glass vials are essentially free of contamination by compounds of interest to this program; the positive values found for methylchloroform and carbon tetrachloride are close to or within the total error of the analytical procedure.

On the other hand, the collectors that were packaged in the standard holders and envelopes (Table 5) definitely contained methylchloroform and showed some evidence for several other compounds. Although appreciable concentrations of 1,2-dichloroethane are indicated by the results, the retention times of the subject chromatographic peaks were sufficiently at variance with those of the standards to cause some question as to the identification of the detected compound(s) as 1,2-dichloroethane. A similar problem exists for the trichloroethylene and tetrachloroethylene results for these samples. With these compounds, ECD responses were obtained at approximately the right retention times, but the corresponding PID responses were not present. These spurious peaks were not seen in subsequent badge analyses. Additional blanks were run as a matter of course in the chamber tests, where badges similar to the ones cited in Table 5 were employed. These continued to indicate methylchloroform similar to that shown in Table 5 but no other compounds were observed in significant amounts.

ANALYTICAL METHODOLOGY

Thermal Desorption

Nearly every sample obtained from the chamber tests was analyzed by thermal desorption as well as by liquid desorption. Also, several additional samples were prepared and analyzed by thermal desorption. Results of these trials proved to be very nonreproducible, and apparent recoveries obtained by the thermal desorption technique were always much less than were obtained by the liquid desorption method.

Detection Limits

Approximate detection limits for gas samples are shown in Table 2. With liquid desorbed badge samples these same values indicate the approximate detection limits for an exposure time of three hours.

TABLE 4. DUPONT BADGE BLANKS
(SC-Series)[a]

Compound	Badge No. SC-1	SC-6	SC-8	Solvent ng/ml
	Contamination, ng/badge			
Chloroform	< 5	< 5	< 5	< 5
1,2-Dichloroethane	<180	<180	<180	<180
Methylchloroform	0[b]	7.1	5.2	23
Carbon Tetrachloride	0.1	0[b]	0.3	0.8
Trichloroethylene	< 4.2	< 4.2	< 4.2	< 4.2
Tetrachloroethylene	< 7.7	< 7.7	< 7.7	< 7.7
Benzene	< 10	< 10	< 10	< 10
Chlorobenzene	< 18	< 18	< 18	< 18
Dioxane	< 67	< 67	< 67	< 67
Vinylidene Chloride	< 29	< 29	< 29	< 29

(a) Collectors supplied in glass vials.
(b) Sample peak slightly smaller than solvent correction.

TABLE 5. DUPONT BADGE BLANKS
(EB-Series)[a]

Compound	Badge No. EB-20	EB-21	EB-22	Solvent ng/ml
	Contamination, ng/badge			
Chloroform	< 5	< 5	< 5	< 5
1,2-Dichloroethane	—— Interfering Contaminant[b] ——			<180
Methylchloroform	45	56	19	23.5
Carbon Tetrachloride	0.6	0.1	0.1	2.4
Trichloroethylene	0.3[b]	0[b]	0[b]	11.4
Tetrachloroethylene	26[b]	13[b]	0.3[b]	11
Benzene	<10	<10	<10	<10
Chlorobenzene	<18	<18	<18	<18
Dioxane	<67	<67	<67	<67
Vinylidene Chloride	<29	<29	<29	<29

(a) Collectors supplied in normal holders and envelopes.
(b) Interfering contaminants with ECD retention times close to subject compounds; corresponding PID peaks for trichloroethylene and tetrachloroethylene not present.

CHAMBER TESTS

Chamber tests of badge performance were run at various concentrations, exposure times, and relative humidities. Air flow velocities were 80 to 120 fpm for all experiments. A summary of conditions employed for these runs is given in Table 6.

Temperature and air velocity effects were not assessed directly, but are discussed in Section 3 of this report.

Sources of Variation--

Table 7 shows a summary of the results of the chamber tests. Data in this table are presented in terms of the relative responses (badge concentration/gas phase TWA*), with triplicate sets of badges being underlined and with corresponding TWA's displayed below the lines for each set. A cursory examination of these data reveals considerable scatter in the relative responses. Runs 6 and 8, however, stand alone. In these two runs, the relative humidity was greater than 80 percent, and analysis of the data (see Appendix C) indicates that these results are statistically different from the results of the other runs.

One possibility that was examined to explain the observed variations is that these variations are due to concentration effects. Table 8 (Column 1) shows the r^2 (index of determination) values obtained when an attempt is made to correlate the observed responses with gas phase TWA values for each run (excluding runs 6 and 8). Obviously there is only very weak correlation at best. (Particular attention should be given to the data for the chlorinated hydrocarbons, where the data sets are more complete.)

However, a closer examination of the data reveals that when a relatively high response is observed for one chemical, the responses for the others also tend to be relatively high. Indeed, correlation of the responses for one chemical with those of any other shows quite high values of r^2. This suggests that the variations observed may be largely due to variations in the devices (e.g., sampling rates). To obtain an estimate of this effect, the individual responses were correlated with mean response values for each badge, with the results shown in Table 8 (Column 2). For this purpose, mean values of the chlorinated hydrocarbon response values were taken as references. The results suggest a strong correlation between individual responses and badge means for all chemicals. A measure of the contribution of this effect to the overall average response for a given chemical and its standard deviation can be obtained by normalizing the data with respect to the badge means. When this is done, the new average response values are changed very little (Table 8, Columns 3 and 4), but the standard deviations are improved by an average of 58 percent for the chlorinated hydrocarbons and 52 percent for all chemicals.

The apparent magnitude of the contribution of the sampling rate variations to overall data variance is much larger than suggested by Lautenberger

* Time weighted average concentration

TABLE 6. SUMMARY OF CHAMBER CONDITIONS

Run Number	Nominal TWA, ppbv	Relative Humidity, %	Time, min.
2	4 - 16	7	225
3	3 - 48	72	240
4	11 - 38	7	240
5	0.2 - 0.5	7	1260
6	1.1 - 3	80	1080
7	1.7 - 3.3	11	1140
8	2.2 - 5.7	92	1200
9	1.6 - 10	7	1260

TABLE 7. SUMMARY OF BADGE RESPONSES[a]

Chemical	Run/Badge 21	22	23	31	32	33	41	42	43	51	52	53	61	62	63	71	72	73	81	82	91	92	93
Chloroform	0.99	0.69	1.86	0.90	0.99	0.76	1.46	1.01	0.99	0.75	0.90	0.79	0.45	0.42	0.44	0.84	0.94	0.86	0.43	0.46	0.66	0.79	0.81
		4.6			9.6			11.1			0.47			1.7			1.7			2.2		1.6	
Methylchloroform	1.08	0.83	1.94	1.03	1.11	0.77	1.89	1.27	1.30	0.88	0.97	0.95	0.42	0.68	0.98	1.18		1.31			1.13	1.25	1.30
		7.0			10.4			12.1			4.3			3.1			2.2			4.0		9.3	
Carbon Tetrachloride	0.66	0.47	1.28	0.85	0.89	0.60	1.28	0.86	0.83	0.78	0.81	0.84	0.27	0.27	0.29	0.42	0.42	0.49	0.28	0.29	0.52	0.59	0.61
		9.2			13.8			17.0			0.037			2.4			2.2			2.8		1.6	
Trichloro-ethylene	0.95	0.68	1.78	1.07	1.08	0.73	1.53	0.99	0.97	1.38	1.45	1.51	0.64	0.67	0.68	0.70	0.77	0.82	0.56	0.35	0.90	0.99	1.02
		9.7			18.6			21.2			0.32			1.9			2.0			2.3		1.9	
Tetrachloro-ethylene	0.99	0.71	1.82	1.22	1.24	0.72	1.70	1.08	1.05	0.96	0.95	0.94	0.35	0.44	0.42	0.61	0.60	0.95	0.36	0.38	0.70	0.74	0.81
		16.0			31.1			35.0			0.34			1.5			2.4			3.4		3.8	
Benzene	1.03	0.82	1.85																0.35	0.34	0.71	0.65	0.73
		3.7																		5.8		2.4	
Chlorobenzene				0.86	0.81	0.51	1.55	1.03	0.98				0.84	0.74	0.83				0.50	0.52			
					48.7			37.7						1.1						2.4			

(a) Key to table format:

(1) First digit of run/badge ID = run ID; second digit = badge number

(2) Responses are coded as $\frac{\text{apparent badge concentration/gas phase TWA}}{\text{gas phase TWA (ppbv)}}$

(3) Blanks indicate no usable data obtained.

TABLE 8. DATA CORRELATIONS OF BADGE RESPONSES

Chemical	Index of Determination, r^2		$\bar{R}$	SDev	$\bar{R}$	SDev
	Response X TWA	Response X Mean	Uncorr.		Corr.	
Chloroform	0.11	0.91	0.94	0.29	0.96	0.12
Methylchloroform	0.06	0.76	1.19	0.31	1.19	0.18
Carbon Tetrachloride	0.24	0.93	0.73	0.26	0.71	0.11
Trichloroethylene	0.00	0.79	1.07	0.32	1.05	0.13
Tetrachloroethylene	0.25	0.96	0.98	0.33	0.96	0.11
Benzene	(0.42)[a]	(0.93)	(0.97)	(0.45)	(0.94)	(0.17)
Chlorobenzene	(0.54)	(0.69)	(0.96)	(0.34)	(1.07)	(0.28)

(a) Parentheses indicate limited data base.

(2). We therefore have re-examined 30 of the diffuser plates taken from badges used on this program. In these measurements, the thicknesses of the plates and the volumes of the channels were determined, and the ratio of channel area to channel length was then calculated for each plate. The coefficient of variation for these measurements was 0.055, which is in good agreement with Lautenberger's estimate of 0.05. Thus the observed variations in apparent sampling rate must be due to some factor other than A/L, and may indicate poor seals between the plates for those badges showing very high responses.

The remaining variations in the data can be attributed largely to analytical error. Each response ratio is derived from analysis of two different samples, badge and gas, and the precision associated with each is approximately $\pm$ 5 percent. Exceptions to this appear in the cases of methylchloroform, benzene and chlorobenzene. With the latter two chemicals, there is only limited data, however, because of analytical problems encountered. With methylchloroform, and with benzene to a lesser extent, spurious contamination of laboratory air, standards, and solvents was a frequent problem and some of the observed variation with these chemicals could be due to this contamination.

Sampling Rates--

Average response ratios shown in Table 7 suggest that, for the most part, the sampling rates recommended by the manufacturer are reasonably accurate. The two exceptions to this are found in the cases of methylchloroform and carbon tetrachloride. In the former case, our estimated sampling rate (Table 1) is 1.2 times higher than the DuPont rate. Thus, use of our estimated rate would yield an average response ratio of about 1.0 for methylchloroform. With carbon tetrachloride, however, no such suggestion can be made and the consistently low response for carbon tetrachloride must be attributed to some factor other than an incorrect diffusion coefficient. The observations might be attributed to an erroneous desorption efficiency, but such would require an unreasonably low (ca. 50 percent) desorption efficiency.

In several of the chamber experiments it was possible to estimate sampling rates directly from the measured rates of loss of each chemical in the chamber. In doing this it was assumed that the only sources of loss were (1) sorption by the three badges and (2) sampling for gas analysis. The rate of change in concentration for each species in the chamber is thus

$$V \frac{dC}{dt} = F_m C_m - F_s C - 3F_b C$$

where F_m is the makeup rate, C_m is the concentration in the makeup gas, F_s is the gas sampling rate, F_b is the badge sampling rate, and V is the chamber volume. Inasmuch as $F_m = F_s$ and $C_m = 0$,

$$\ln(C/C_o) = -(F_s + 3F_b)t/V$$

and a plot of ln C/C_o versus t can be used to estimate F_b. Sampling rates estimated for runs 6, 7, 8, and 9 are shown in Table 9.

TABLE 9. ESTIMATED SAMPLING RATES
(cc/min)

Chemical	Run Number			
	6[a]	7	8[a]	9
Chloroform	39	56	30	66
Methylchloroform	31	37	28	70
Carbon Tetrachloride	44	50	25	66
Trichloroethylene	55	56	50	64
Tetrachloroethylene	57	63	29	61
Benzene	69	35	61	76
Chlorobenzene	56	35	55	46

[a]High humidity tests.

Although the sampling rates shown in Table 9 are only estimates, they appear to correlate with the observed responses for these runs shown in Table 7.

Laboratory Air Tests--

In addition to the chamber tests, two exposure runs were made in the laboratory to examine the responses of the badges in a "real" atmosphere and to verify the velocity effect. In the first experiment, one badge (A) was suspended in an open area in the lab; one badge (B) was suspended in front of a small blower; and the third badge (C) was worn by a person working in the lab. Hourly readings of air composition and air velocity near each badge were taken. Results are shown in Table 10. The TWA values found were ca. one half those in the air except for benzene which was 40% higher than the air value.

In the second laboratory air experiment, four badges were exposed for a period of 8 hours. Two of these (A and AA) were suspended in front of a small blower and the other two (B and BB) were each suspended within an open beaker to minimize convective transport. Results of this experiment are shown in Table 11. The suspension of the badges within beakers for this experiment does not totally inhibit transport to the badges, but rather limits transport by redefinition of the diffusion path. For the beaker size and geometry that was used we estimate that the overall sampling rate should have been decreased by about 50 percent. Values reported in Table 11 are in reasonably good agreement with this anticipated reduction and shows the importance of air velocity on the results. The results in Runs A and AA are in good agreement with the air results (~20%).

Precision and Accuracy--

The precision and accuracy to be associated with the chamber studies are related to a number of factors as indicated in Table 12. Estimated coefficients of variation given in this table are based on repeatability of analysis, estimated temperature and velocity effects, and apparent variations in sampling rates. Analysis of the actual data given in Table 7, using the nomenclature of Lautenberger, et al (2), yields similar values for the overall accuracy and slightly lower values for the overall mean coefficients of variation. Results of this analysis are shown in Table 13. These data again reflect the earlier observation that improved reference sampling rates, especially in the case of carbon tetrachloride, should improve the overall accuracy considerably. If the data are normalized, as discussed earlier, the overall accuracy is improved by an average of 0.25 ± 0.09 for the five chlorinated hydrocarbons, again stressing the contribution of variation in the badge sampling rate.

TABLE 10. FIRST LABORATORY AIR EXPERIMENT[a,b]

Compound	TWA Concentration, ppbv			
		Badge No.		
	Air	A	B	C
Chloroform	1.2	-	0.70	0.79
Methylchloroform	>110	>300	>300	>300
Carbon Tetrachloride	0.54	0.20	0.29	0.26
Trichloroethylene	7.6	4.5	5.3	5.5
Tetrachloroethylene	3.4	1.7	2.0	2.1
Benzene	6.3	8.1	8.6	9.3
Chlorobenzene	0.26	<0.5	<0.5	<0.5

(a) Exposure time = 6 hours; RH = 28%; T = 23.5 C.
(b) Velocities: A = 20 fpm; B = 125 fpm; C = 3 hr @ 15 fpm plus 3 hr @ 180 fpm.

TABLE 11. SECOND LABORATORY AIR EXPERIMENT[a,b]

Compound	TWA Concentration, ppbv				
		Badge No.			
	Air	A	AA	B	BB
Chloroform	1.0	0.73	0.81	-	-
Methylchloroform	900	690	940	500	609
Carbon Tetrachloride	1.05	0.85	0.98	0.50	0.52
Trichloroethylene	32	25	29	18	18
Tetrachloroethylene	11	8.1	9.2	4.3	4.7
Benzene	7.2	5.3	8.7	2.1	1.8
Chlorobenzene	0.13	<0.3	0.3	<0.3	<0.3

(a) Exposure time = 8 hours; RH = 21%; T = 22.5 C.
(b) Velocity: A & AA = 120 fpm; B & BB $\approx$ 0.

TABLE 12. FACTORS AFFECTING PRECISION AND ACCURACY

Source	Estimated CV[a]	Affected Measure	
		Precision	Accuracy
1. Analysis Method			
a. Solvent blank	0.05	(X)[b]	(X)[b]
b. Desorption efficiency	0.10		X
c. Sample analysis	0.05	X	X
2. Sampling Conditions			
a. Velocity	0.04		X
b. Temperature	0.03		X
3. Device Characteristics			
a. Badge blank	0.05	(X)[b]	(X)[b]
b. Sampling rate	0.055	X	X
Totals		0.11 - 0.22	0.28 - 0.38

(a) Coefficient of variation = standard deviation/mean.
(b) Maximum contribution of blanks; if blank is much smaller than sample, contribution will be less.

TABLE 13. EXPERIMENTAL PRECISION AND ACCURACY

Chemical	Mean CV[a]	Mean Bias[b]	Overall Accuracy[c]
Chloroform	0.15	-0.11	0.41
Methylchloroform	0.15	0.14	0.45
Carbon Tetrachloride	0.16	-0.30	0.63
Trichloroethylene	0.17	0.03	0.37
Tetrachloroethylene	0.22	-0.06	0.51
Benzene	(0.10)[d]	(-0.21)	(0.42)
Chlorobenzene	(0.26)	(-0.09)	(0.61)

(a) Based on data in Table 7, excluding runs 6 and 8.
(b) Group mean value of run mean deviation from response of unity.
(c) Overall accuracy ≡ ± (absolute mean bias + 2 mean CV).
(d) Limited data.

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APPENDIX A

EFFECT OF AIR VELOCITY ON SAMPLING RATE

VELOCITY EFFECT

The physical mechanism whereby passive monitors achieve effectively constant volumetric sampling rates is determined by the use of a well-defined diffusion path between the collection medium and the external environment. The relationships generally cited for calculation of badge sampling rates assume that the gas phase concentration of a given species is at the environmental level (C_∞) at the outer surface of the collection medium. This assumption is never exactly correct but is compensated for by experimental determinations of sampling rates by the manufacturers. Such rates, however, are useful only when the external gas velocity is sufficient to bring the gas species to the outer surface of the badge at least as fast as they are depleted by diffusion to the collection medium. This importance of the gas velocity has been demonstrated experimentally by Lautenberger, et al (2), at DuPont and, as we show below, their results are consistent with a simple aerodynamic model of mass transfer to the badge.

Consider the system indicated by Figure A-1 where a collector is separated from the external air by a series of channels having length x and a total open area of A_o. Flow of air over the surface of the channels (badge) will tend to result in the formation of a relatively stagnant boundary layer between the badge and the bulk air. Mass fluxes from the bulk air to the surface of the badge (J_2) and from the surface to the collector (J_1) are given by Fick's first law

$$J_1 = D \left(\frac{dC}{dx}\right)_{o \to x} = D \frac{C_x - C_o}{x} \qquad (A1)$$

and

$$J_2 = D \left(\frac{dC}{dx}\right)_{x \to \delta} = D \frac{C_\infty - C_x}{\delta} \qquad (A2)$$

where D is the diffusion coefficient for a given species. If the total face area of the badge is A_b and C_o is taken to be zero, the mass transfer rates can be written as

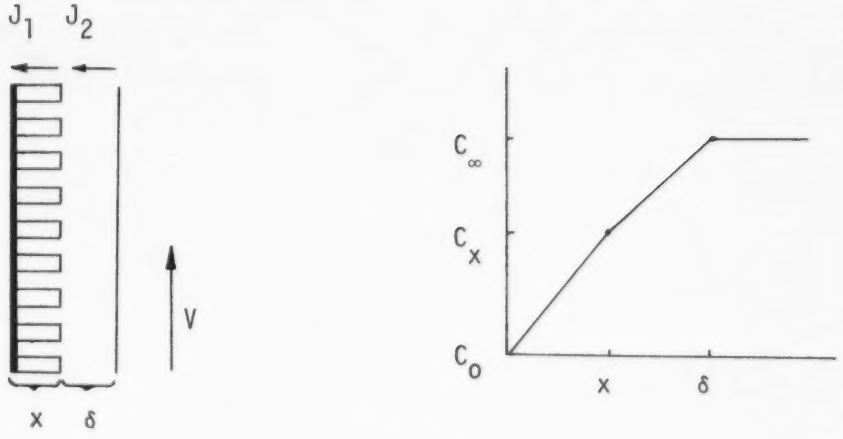

Figure A-1. Boundary Layer Over Badge Surface

$$\dot{m}_1 = \frac{A_o}{x} D C_x \tag{A3}$$

and

$$\dot{m}_2 = \frac{A_b}{\delta} D (C_\infty - C_x) \tag{A4}$$

Recognizing that $A_o/A_b = \varepsilon$, the effective porosity of the badge surface, and that, in a steady-state sampling condition, $\dot{m}_1 = \dot{m}_2$

$$\frac{C_x}{C_\infty - C_x} = \frac{x}{\varepsilon\delta} \tag{A5}$$

or

$$\frac{C_x}{C_\infty} = \frac{x/\varepsilon\delta}{1+x/\varepsilon\delta} \tag{A6}$$

Now δ is a function of the air velocity and the badge dimensions (e.g., see R. B. Bird, W. E. Stewart and E. N. Lightfoot, Transport Phenomena, John Wiley and Sons, Inc., New York, 1960, Chapters 4 and 19).

$$\delta = 3.46 \left(\frac{\mu \ell}{V\rho}\right)^{1/2} \tag{A7}$$

where μ is the viscosity, ℓ is the distance from the leading edge of the surface, and ρ is the density of the air. Using the dimensions of the DuPont badge,

$$x = 0.35 \text{ cm}, \ \varepsilon = 0.3, \ \ell = 0.5 \text{ cm}$$

$$\rho = 1.2 \times 10^{-3} \text{ g/cm}^3, \ \mu = 1.85 \times 10^{-4} \text{ poise}$$

$$(V = \text{cm/sec})$$

and

$$\frac{C_x}{C_\infty} = \frac{0.36 \, V^{1/2}}{\varepsilon + 0.36 \, V^{1/2}} \tag{A8}$$

Inasmuch as it is normally assumed that $C_x \simeq C_\infty$, equation (A8) indicates the absolute accuracy of the sampling rate as a function of velocity. A plot of this function is shown in Figure A-2.

The need for calibration of effective sampling rates by the manufacturer is made obvious by Figure A-2; C_x approaches C only at very high velocities. It should be noted, however, that C_x is relatively independent of velocity above some arbitrary minimum of say 50 fpm. Below about 50 fpm and certainly below 30 fpm, the steady-state sampling rate is a serious function of velocity. This behavior is essentially the same as noted by Lautenberger, et al, with the exception that they assumed a constant rate at high velocities.

From a practical viewpoint, Figure A-2 illustrates a potentially serious fault of the passive monitor. Although velocities of 50 to 100 fpm are routinely generated by movement of an active worker, such velocities may not be attained by an office worker or a subject not engaged in vigorous activity. Indeed, velocity measurements conducted at a wide variety of sites in our laboratories generally showed velocities below 30 fpm unless either (a) direct exposure to ventilation or (b) movement at walking speeds was involved. This problem may be further compounded by the shielding effect of the body and clothing when the badge is worn close to the body (as opposed to being attached to an extremity).

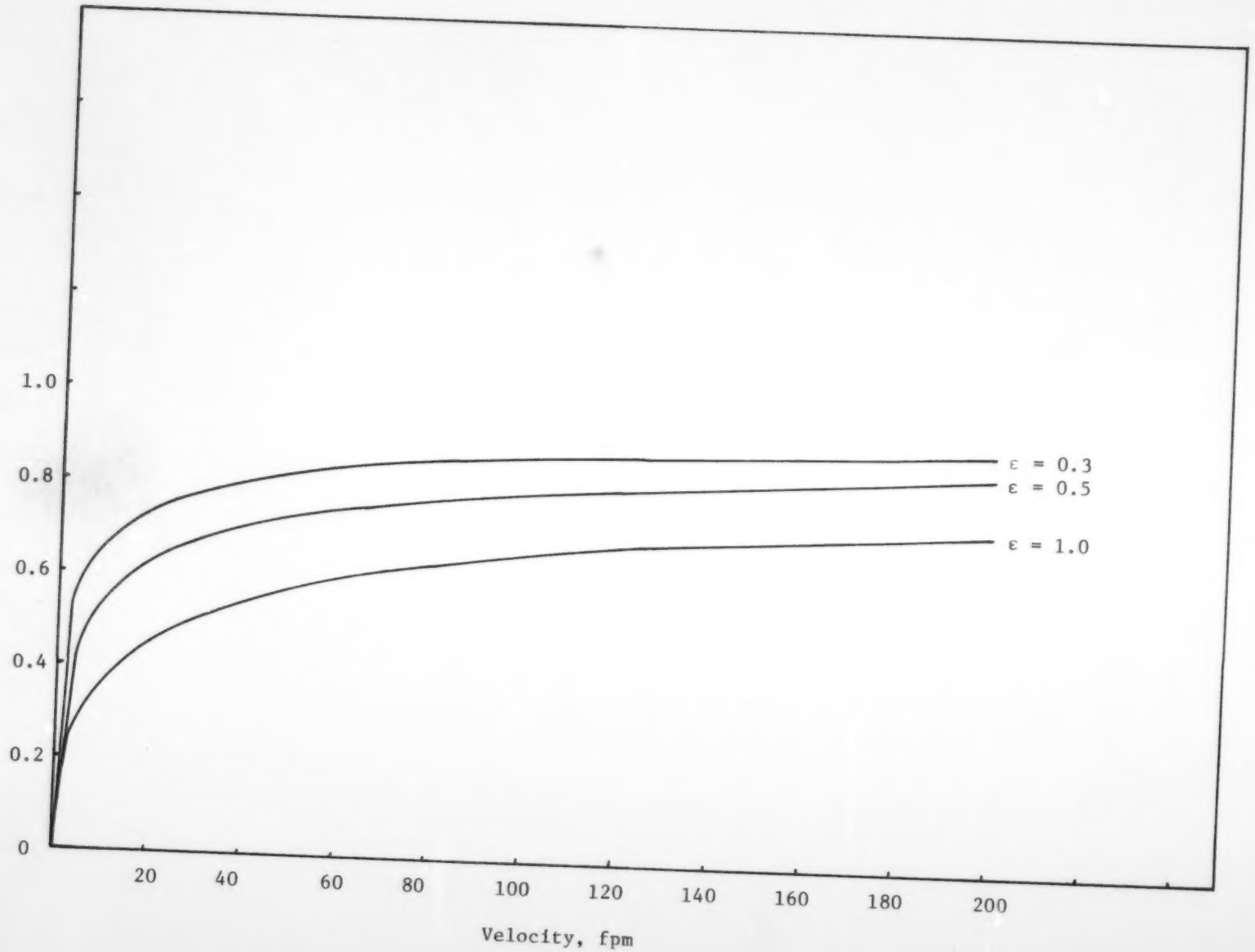

FIGURE A-2. EFFECT OF AIR VELOCITY ON SAMPLING RATE

APPENDIX B

CHAMBER RUN PROCEDURE

BADGE EXPOSURE RUNS

1. 200-l chamber preparation

A. Flush chamber with clean air and adjust humidity

B. Adjust maintenance flow to 80 cc/min to maintain 1" water pressure on the chamber at a 50 cc/min sampling rate

C. Chamber background checked by G. C.

D. Chamber injected with proper amount of chemical cocktail and checked by G. C.

2. Badges readied for chambers

A. Badges are weighed and packages labeled

B. Stainless steel holder cleaned and flushed with clean N_2

C. Stainless steel holder loaded with badges while N_2 flowing through tube is sealed

D. Holder is then placed in chamber and badges exposed

E. G. C. samples run about each hour to follow concentration in chamber.

3. New extraction solvent (95 percent MEOH, 5 percent CS_2) made and then checked by G. C. for background before use.

4. Badge removal from stainless steel holder

A. Stainless steel holder is opened in a large poly bag filled with clean N_2

B. Extraction bottles are preloaded with 1 cc of solvent

C. With badge roller, badge is loaded into 1 dram vial

D. Blank badge carried through same procedure

E. Extraction is done overnight

F. Analysis is done by G. C. using 1 μl injection of blank solvent, sample, 2.5 standard

5. Weight of badge determined by now weighing badge holder.

APPENDIX C

PRELIMINARY STATISTICAL ANALYSIS

PRELIMINARY STATISTICAL ANALYSIS OF RESPONSE RATIO DATA

Introduction

The following section describes the statistical analyses which were performed on the response ratio data collected during this experiment. The performance ratios of five different chemicals were studied.* The experimental design was a single factor (Runbadges/humidity conditions) with three replications taken in each group.

The basic statistical model applicable to this design is given by Equation C-1 below.

$$X_{ij} = \mu_i + \varepsilon_{ij} \quad , \quad \begin{matrix} i = 1, 2, \ldots, 8 \\ j = 1, 2, 3 \end{matrix} \quad . \qquad \text{(C1)}$$

The variable X_{ij} represents the performance ratio measured on the j^{th} replication in the i^{th} treatment group. The parameter μ_i is the average performance ratio for the i^{th} treatment group. The ε_{ij} are random error terms which account for all uncontrolled sources of experimental error. In general the $\{\varepsilon_{ij}\}$ are assumed to be independent random variables distributed normally with mean zero and constant variance.

The primary objective of the statistical analyses was to test the null hypothesis H_0 versus the alternative hypothesis H_A given by

$$H_0: \mu_1 = \mu_2 = \ldots = \mu_8$$

versus

$$H_A = \mu_1 = \mu_j \text{ for some } i, j - 1, 2, \ldots, 8 \quad . \qquad \text{(C2)}$$

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*Data sets for benzene and chlorobenzene were relatively incomplete and were not included in this analysis.

That is, the primary objective of the statistical analyses was to test whether or not the average response ratio is the same for all eight groups. Separate analyses were performed for each of the five chemicals for which reasonably complete data sets were available.

Statistical Analyses

The data were initially transferred from the laboratory data sheets onto a computer file. The data were than checked for accuracy, and they are listed in Table C-1 (values of -9 indicate missing data). Summary statistics (means and standard deviations for the three replications in each treatment group) were calculated, and they are presented in Table C-2.

The test of the hypotheses given in (C-2) is carried out formally by performing a one-way analysis of variance. As a result of the one-way analysis of variance an analysis of variance table can be constructed from which an F-statistic can be calculated (see Reference C-1, Chapter 10). The null hypothesis is accepted or rejected based on the value of the F-statistic.

The analysis of variance procedure and the F-test are based on the assumption that the random error terms have the same variance within each treatment group. Therefore a Bartlett's test (see Reference C-1, pp. 296-298) was performed to check this assumption. In all cases Bartlett's test indicated that these variances were not equal across the groups. However, the same number of replicates were used in each group (i.e., 3) which is known as a balanced design. The assumption of equal variances is not critical for balanced designs and therefore the unequal variances were ignored in the subsequent analyses.

Runbadge groups 5 and 7* (high humidity tests) were known to have encountered experimental problems and therefore the analyses of variance and subsequent tests were performed in two ways: both with Runbadge groups 5 and 7 and without Runbadge groups 5 and 7. The resulting analysis of variance tables for each of the five chemicals both with and without groups 5 and 7 are presented below along with a graphical display of the group means and their associated 95 percent error limits. The first set of tables include groups 5 and 7 and the second set of tables do not.

Summary and Conclusions

The results of the analyses of variance are summarized in Table C-3 below. The symbol R indicates the null hypothesis in (C-2) was rejected at the 5 percent significance level and an NR indicates the null hypothesis was not rejected. For these data the null hypothesis can be rejected at the 5 percent level of significance if the F-statistic exceeds 2.70.

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*Actual run numbers were decreased by one for group numbers used in this analysis, i.e., groups 5 and 7 are runs 6 and 8, respectively.

TABLE C-1. RAW DATA

RUNBADGE 115	CHEMICAL 115	REP 115	X 115
1.	1.	1.	0.99000
1.	1.	2.	0.69000
1.	1.	3.	1.86000
2.	1.	1.	0.90000
2.	1.	2.	0.99000
2.	1.	3.	0.76000
3.	1.	1.	1.46000
3.	1.	2.	1.01000
3.	1.	3.	0.99000
4.	1.	1.	0.75000
4.	1.	2.	0.90000
4.	1.	3.	0.79000
5.	1.	1.	0.45000
5.	1.	2.	0.42000
5.	1.	3.	0.44000
6.	1.	1.	0.84000
6.	1.	2.	0.94000
6.	1.	3.	0.86000
7.	1.	1.	0.43000
7.	1.	2.	0.46000
8.	1.	1.	0.66000
8.	1.	2.	0.79000
8.	1.	3.	0.81000
1.	2.	1.	1.08000
1.	2.	2.	0.83000
1.	2.	3.	1.94000
2.	2.	1.	1.03000
2.	2.	2.	1.11000
2.	2.	3.	0.77000
3.	2.	1.	1.89000
3.	2.	2.	1.27000
3.	2.	3.	1.30000
4.	2.	1.	0.88000
4.	2.	2.	0.97000
4.	2.	3.	0.95000
5.	2.	1.	0.42000
5.	2.	2.	0.68000
5.	2.	3.	0.98000
6.	2.	1.	1.18000
6.	2.	2.	1.24500
6.	2.	3.	1.31000
7.	2.	1.	-9.00000
7.	2.	2.	-9.00000
8.	2.	1.	1.13000
8.	2.	2.	1.25000
8.	2.	3.	1.30000
1.	3.	1.	0.66000
1.	3.	2.	0.47000
1.	3.	3.	1.26000
2.	3.	1.	0.85000
2.	3.	2.	0.89000
2.	3.	3.	0.60000
3.	3.	1.	1.28000
3.	3.	2.	0.86000
3.	3.	3.	0.83000
4.	3.	1.	0.78000

TABLE C-1. (Continued)

4.	3.	2.	0.81000
4.	3.	3.	0.84000
5.	3.	1.	0.27000
5.	3.	2.	0.27000
5.	3.	3.	0.29000
6.	3.	1.	0.42000
6.	3.	2.	0.42000
6.	3.	3.	0.49000
7.	3.	1.	0.28000
7.	3.	2.	0.29000
8.	3.	1.	0.52000
8.	3.	2.	0.59000
8.	3.	3.	0.61000
1.	4.	1.	0.95000
1.	4.	2.	0.68000
1.	4.	3.	1.78000
2.	4.	1.	1.07000
2.	4.	2.	1.08000
2.	4.	3.	0.73000
3.	4.	1.	1.53000
3.	4.	2.	0.99000
3.	4.	3.	0.97000
4.	4.	1.	1.38000
4.	4.	2.	1.45000
4.	4.	3.	1.51000
5.	4.	1.	0.64000
5.	4.	2.	0.67000
5.	4.	3.	0.68000
6.	4.	1.	0.70000
6.	4.	2.	0.77000
6.	4.	3.	0.82000
7.	4.	1.	0.56000
7.	4.	2.	0.35000
8.	4.	1.	0.90000
8.	4.	2.	0.99000
8.	4.	3.	1.02000
1.	5.	1.	0.99000
1.	5.	2.	0.71000
1.	5.	3.	1.82000
2.	5.	1.	1.22000
2.	5.	2.	1.24000
2.	5.	3.	0.72000
3.	5.	1.	1.70000
3.	5.	2.	1.08000
3.	5.	3.	1.05000
4.	5.	1.	0.96000
4.	5.	2.	0.95000
4.	5.	3.	0.94000
5.	5.	1.	0.35000
5.	5.	2.	0.44000
5.	5.	3.	0.42000
6.	5.	1.	0.61000
6.	5.	2.	0.60000
6.	5.	3.	0.95000
7.	5.	1.	0.36000
7.	5.	2.	0.38000
8.	5.	1.	0.70000
8.	5.	2.	0.74000
8.	5.	3.	0.81000

TABLE C-2. MEANS/STANDARD DEVIATIONS

ROWS: RUNBADGE COLUMNS: CHEMICAL

	1	2	3	4	5
1	1.1800	1.2833	0.8033	1.1367	1.1733
	0.6077	0.5823	0.4236	0.5733	0.5773
2	0.9833	0.9700	0.7800	0.9600	1.0600
	0.1159	0.1778	0.1572	0.1992	0.2946
3	1.1533	1.4867	0.9900	1.1633	1.2767
	0.2658	0.3496	0.2516	0.3177	0.3669
4	0.8133	0.9333	0.8100	1.4467	0.9500
	0.0777	0.0473	0.0300	0.0651	0.0100
5	0.4367	0.6933	0.2767	0.6633	0.4033
	0.0153	0.2802	0.0115	0.0208	0.0473
6	0.8800	1.2450	0.4433	0.7633	0.7200
	0.0529	0.0650	0.0404	0.0603	0.1992
7	0.4450	-9.0000*	0.2850	0.4550	0.3700
	0.0212	0.0000	0.0071	0.1485	0.0141
8	0.7533	1.2267	0.5733	0.9700	0.7500
	0.0814	0.0874	0.0473	0.0624	0.0557

* -9 indicates missing data

The results of these analyses and Table C-3 indicate that there is a significant difference among the eight treatment groups when groups 5 and 7 (high humidity runs) are included in the analysis. The significant difference is apparently due to the low performance ratios obtained for groups 5 and 7. When groups 5 and 7 were removed from the analysis there were no significant differences displayed among the remaining groups. Therefore, high humidity evidently has an effect upon the performance of the badges with the tested chemicals.

TABLE C-3. ANALYSIS OF VARIANCE RESULTS

	Including Groups 5 & 7	Excluding Groups 5 & 7
Chemical 1	R	NR
Chemical 2	NR	NR
Chemical 3	R	NR
Chemical 4	R	NR
Chemical 5	R	NR

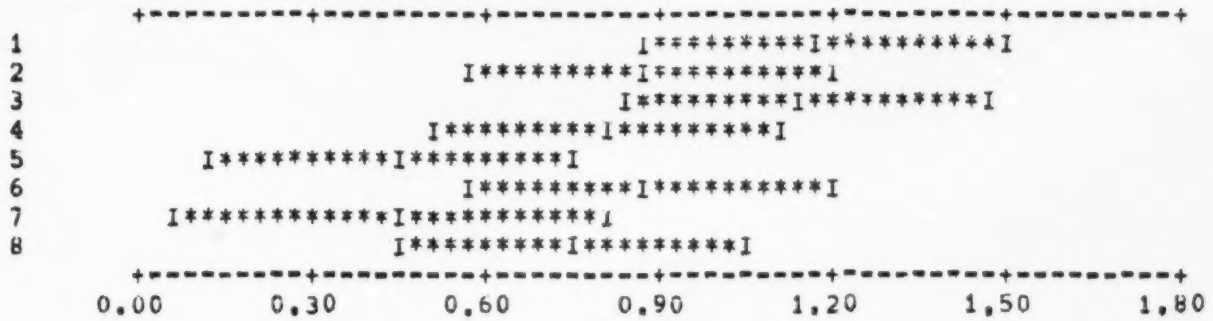
ANALYSIS OF VARIANCE RESULTS INCLUDING GROUPS 5 AND 7

CHEMICAL #1

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF	F-RATIO
FACTOR	7	1.4758	0.2108	3.37
ERROR	15	0.9386	0.0626	
TOTAL	22	2.4144		

INDIVIDUAL 95 PERCENT C. I. FOR LEVEL MEANS
(BASED ON POOLED STANDARD DEVIATION)

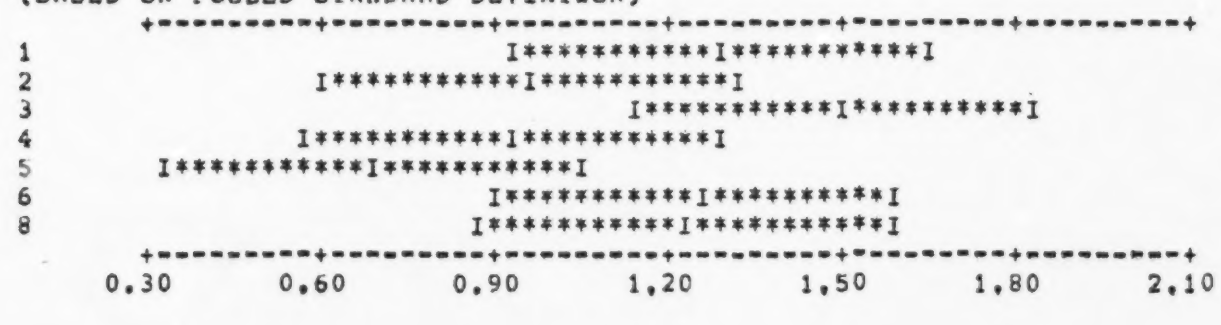


CHEMICAL #2

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF	F-RATIO
FACTOR	6	1.2825	0.2138	2.56
ERROR	14	1.1710	0.0836	
TOTAL	20	2.4535		

INDIVIDUAL 95 PERCENT C. I. FOR LEVEL MEANS
(BASED ON POOLED STANDARD DEVIATION)

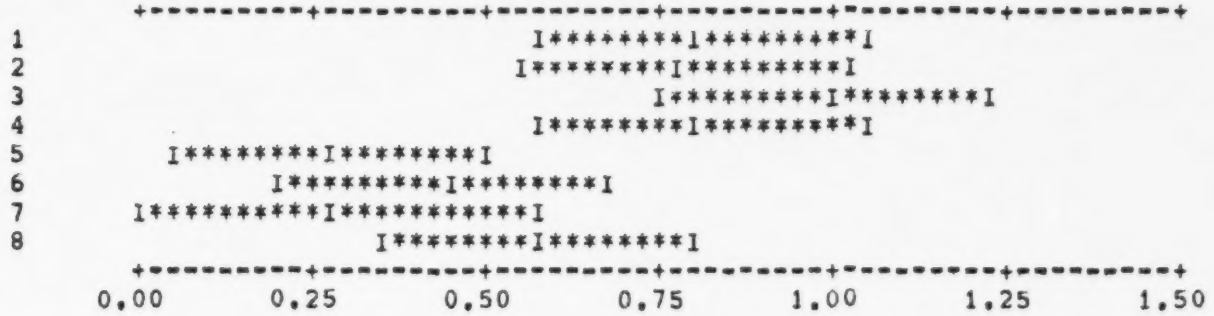


CHEMICAL #3

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF	F-RATIO
FACTOR	7	1.3699	0.1957	5.39
ERROR	15	0.5447	0.0363	
TOTAL	22	1.9146		

INDIVIDUAL 95 PERCENT C. I. FOR LEVEL MEANS
(BASED ON POOLED STANDARD DEVIATION)

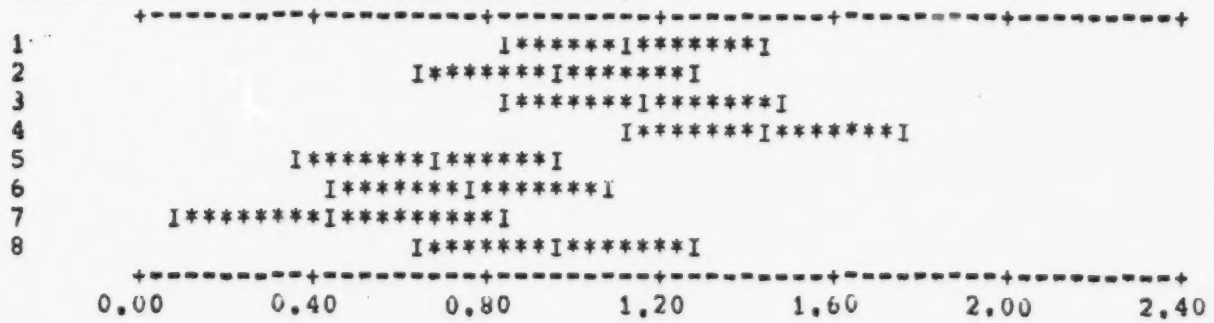


CHEMICAL #4

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF	F-RATIO
FACTOR	7	1.8178	0.2597	3.95
ERROR	15	0.9850	0.0657	
TOTAL	22	2.8027		

INDIVIDUAL 95 PERCENT C. I. FOR LEVEL MEANS
(BASED ON POOLED STANDARD DEVIATION)

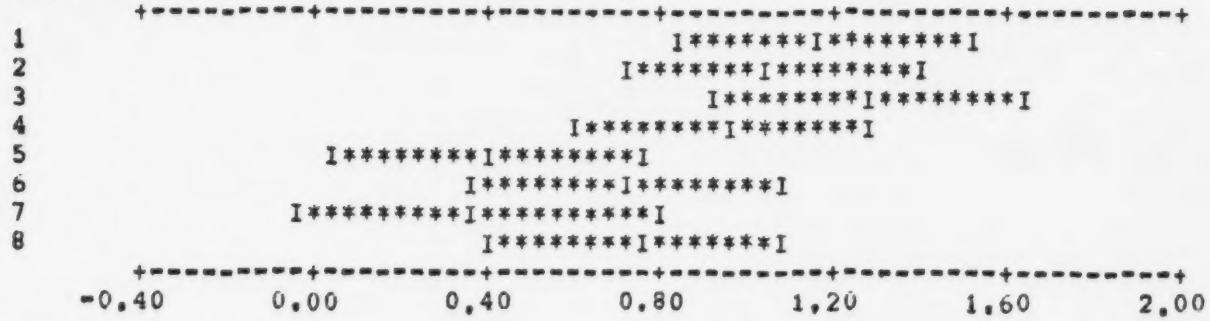


CHEMICAL #5

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF	F-RATIO
FACTOR	7	2.1605	0.3086	3.86
ERROR	15	1.1998	0.0800	
TOTAL	22	3.3603		

INDIVIDUAL 95 PERCENT C. I. FOR LEVEL MEANS
(BASED ON POOLED STANDARD DEVIATION)



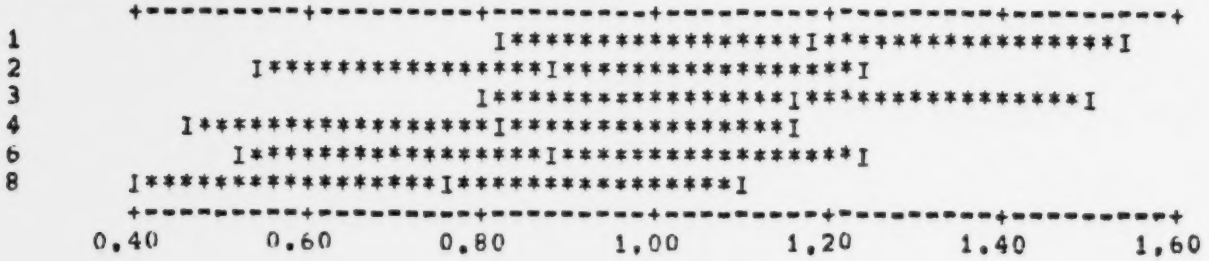
ANALYSIS OF VARIANCE RESULTS EXCLUDING GROUPS 5 AND 7

CHEMICAL #1

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF	F-RATIO
FACTOR	5	0.4822	0.0964	1.23
ERROR	12	0.9377	0.0781	
TOTAL	17	1.4198		

INDIVIDUAL 95 PERCENT C. I. FOR LEVEL MEANS
(BASED ON POOLED STANDARD DEVIATION)

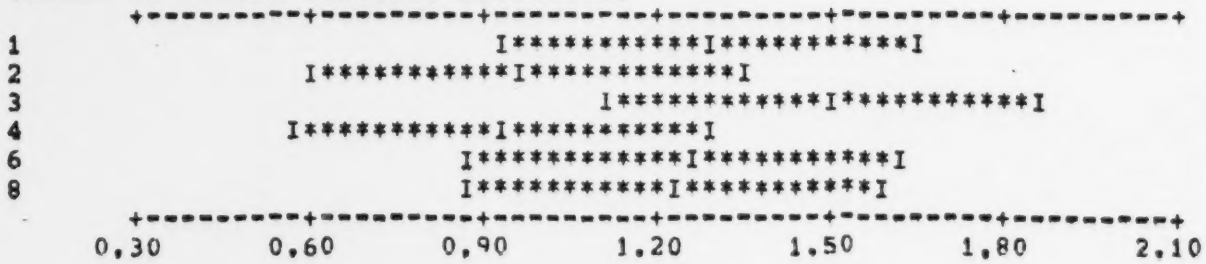


CHEMICAL #2

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF	F-RATIO
FACTOR	5	0.6461	0.1292	1.53
ERROR	12	1.0139	0.0845	
TOTAL	17	1.6600		

INDIVIDUAL 95 PERCENT C. I. FOR LEVEL MEANS
(BASED ON POOLED STANDARD DEVIATION)

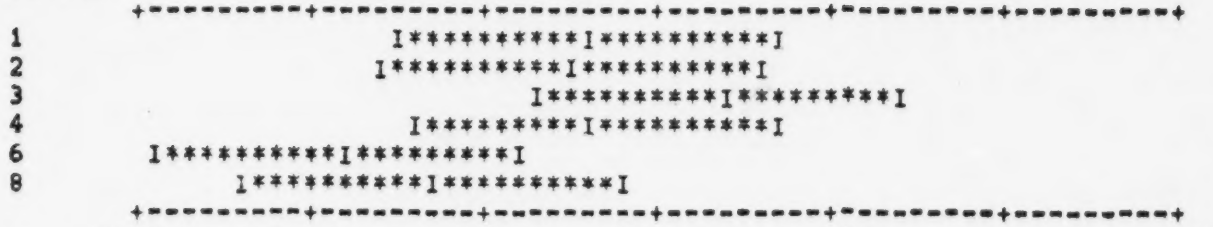


CHEMICAL #3

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF	F-RATIO
FACTOR	5	0.5656	0.1131	2.49
ERROR	12	0.5444	0.0454	
TOTAL	17	1.1100		

INDIVIDUAL 95 PERCENT C. I. FOR LEVEL MEANS
(BASED ON POOLED STANDARD DEVIATION)

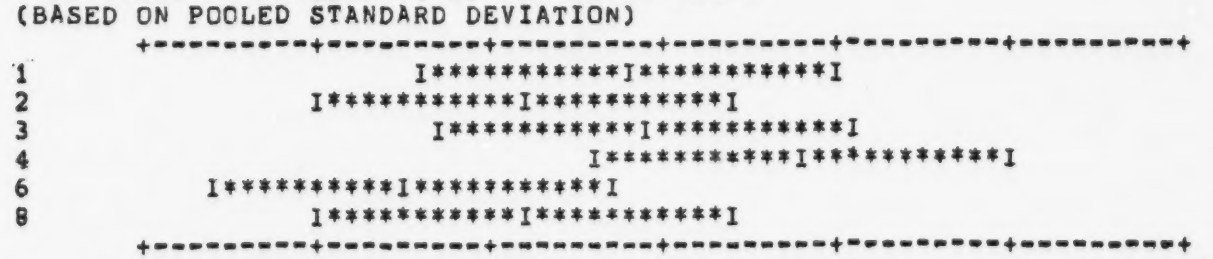


CHEMICAL #4

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF	F-RATIO
FACTOR	5	0.8133	0.1627	2.03
ERROR	12	0.9621	0.0802	
TOTAL	17	1.7754		

INDIVIDUAL 95 PERCENT C. I. FOR LEVEL MEANS
(BASED ON POOLED STANDARD DEVIATION)

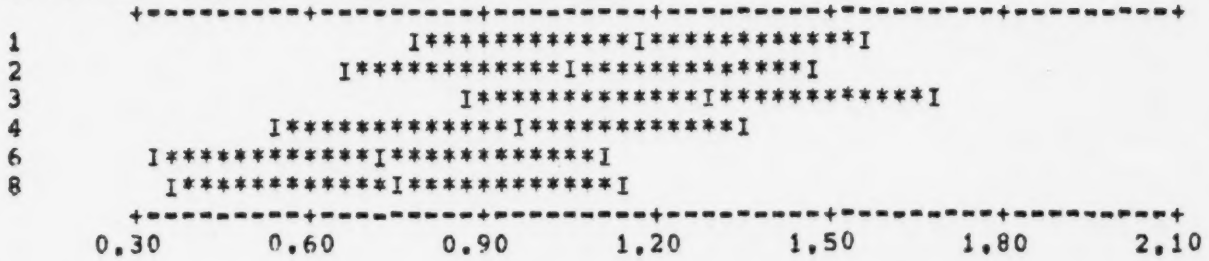


CHEMICAL #5

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF	F-RATIO
FACTOR	5	0.7583	0.1517	1.52
ERROR	12	1.1951	0.0996	
TOTAL	17	1.9535		

INDIVIDUAL 95 PERCENT C. I. FOR LEVEL MEANS
(BASED ON POOLED STANDARD DEVIATION)



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C-1. Snedecor, G. W., and Cochran, W. G., Statistical Methods, The Iowa State University Press, Sixth Edition, 1974.